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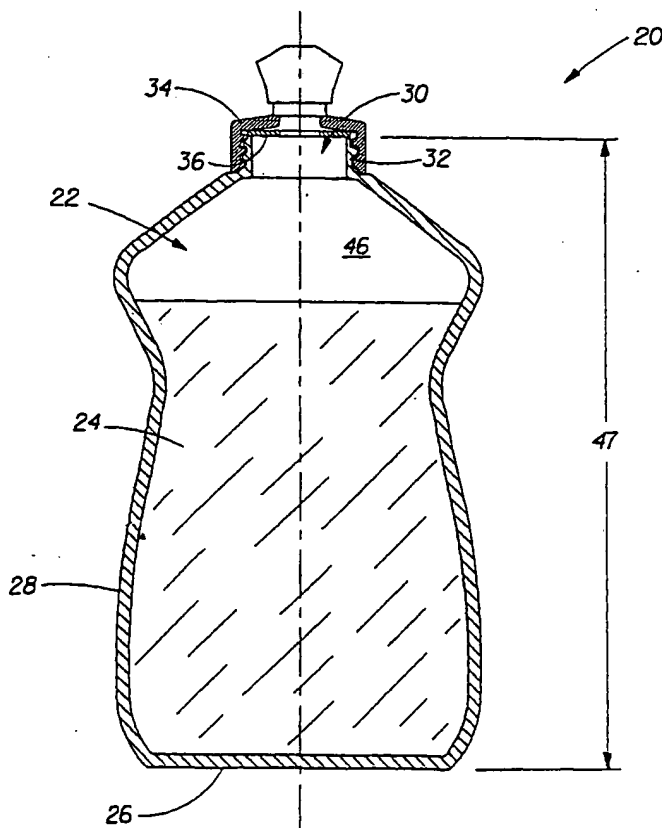
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(54) Title: DETERGENT PACKAGE WITH MEANS TO MASK AMINE MALODOURS



(57) Abstract: A specially-suited package comprising: a container (20) having at least one compartment for storing a liquid (24); a dispensing opening (30) in liquid communication with said at least one compartment; a closure for sealing the opening; and a plastic member impregnated with a perfume composition wherein the plastic member (36) is in communication with said compartment so that upon being released from the plastic member the perfume composition effectively suppresses malodors, particularly those malodors emanating from nitrogenous compounds.

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DETERGENT PACKAGE WITH MEANS TO MASK AMINE MALODOURS

TECHNICAL FIELD

The present invention relates to packages to contain and store liquid or gel compositions such as detergent, cleaning, fabric care, and personal care compositions, particularly liquid detergent compositions suitable for use in manual dishwashing operations. The packages are particularly suited for storing detergent compositions containing malodor-generating compounds and suppressing the malodors emanating from such detergent compositions.

BACKGROUND OF THE INVENTION

Liquid or gel detergent products are widely-used by consumers for a variety of cleaning tasks include the cleaning of hard surfaces (floors, ovens and ranges, countertops), clothing and textile articles, and dishes, cook ware and other kitchen articles. One example of a liquid cleaning product is a light-duty liquid (LDL) detergent composition which is useful for manual dishwashing. Such products are generally formulated to provide a number of widely diverse performance and aesthetics properties and characteristics. First and foremost, liquid and gel dishwashing products must be formulated with types and amounts of surfactants and other cleaning adjuvants that will provide acceptable solubilization and removal of food soils, especially greasy soils, from dishware being cleaned with, or in aqueous solutions formed from, such products. Thus, there is a continuing effort by formulators of liquid dishwashing compositions to incorporate additional components into LDL detergents to provide consumers with improved cleaning benefits.

One example of a component which can improve the cleaning performance of liquid dishwashing detergent compositions is a nitrogenous compound such as a diamine which aids in particular in the cleaning of greasy, hydrophobic soils on dishware or other kitchen articles. However, diamines can also cause extremely potent malodors; for example the unpleasant fragrance associated with permanent kits commonly used to curl hair are generated by diamines. Other nitrogen-containing surfactants and polymers can provide both cleaning and sudsing advantages, but frequently contain amine impurities as by-products in commercial materials. When the composition pH approaches or exceeds the pKa of these amine impurities, the resultant free amine can be malodorous. Consequently, it has been particularly difficult to formulate a malodor-free light duty liquid at pH higher than 8.5.

Amines are just one example of detergent components which provide functional benefits to a liquid detergent composition but are frequently not used because of the undesirable odor

associated with them. Typically malodors associated with detergent products are "masked" (covered up) by placing a perfume composition in the liquid dishwashing detergent, which masks the malodors emanating from the liquid detergent when used in sufficient quantities. These perfumes also provide the added benefit that a desirable fragrance, such as a lemon scent, can be imparted to the liquid detergent product.

However, some malodors cannot be masked simply by adding perfumes to the detergent. For example, when a particular malodor is highly volatile (and therefore diffuses quickly into the air) and/or when a particular malodor is extremely potent, it may be difficult to add a sufficient amount of perfume without giving the liquid dishwashing detergent a strong, perfumed odor. Given the foregoing there is a continuing need to find ways to control the malodors emanating from such cleaning-enhancing components.

Accordingly, a benefit of the present invention is that a package is provided for holding a liquid detergent composition comprising certain nitrogen-containing components which is effective at suppressing the malodors associated with such components. Preferably these malodors are suppressed and neutralized while they are still within the confines of the package, thus preventing the malodors from ever being detected by the consumer.

An additional benefit of the present invention is that it offers a way of imparting two distinct and different fragrant scents to a consumer product. This could be a useful way to convey to a consumer, via an olfactory signal, that a detergent product has two distinct benefits, for example that its detergent composition is both tough on grease, while at the same time is gentle and mild to the skin.

The benefits of this invention can be included in containers for a broad variety of liquid and gel detergent, cleaning, fabric care, and personal care products. Such products may include LDLs, detergents for use in automatic dishwashing machines, laundry detergents, fabric softeners, deodorizers and refreshers, liquid hand soap, shampoo, after shave, cologne and personal deodorants, other personal care compositions, hard surface cleaners, and a variety of other home and personal care products in which odor-emanating compounds like amines may be present and it is desirable to mask or suppress any malodors that they may generate.

SUMMARY OF THE INVENTION

It has now been determined that when a liquid or gel (hereinafter referred to as liquid) composition such as a liquid dishwashing detergent which contains malodor-generating compounds like amines is stored in a package constructed according to the present invention, then the odors

typically associated with the malodor-generating compounds are effectively suppressed by neutralization, modification, or masking and thus not physically sensed by the consumer. This specially-suited package comprises: a container having at least one compartment for storing a liquid; a dispensing opening in liquid communication with said at least one compartment; a closure for sealing the opening; and a plastic member impregnated with a perfume composition, wherein the plastic member is in communication with said compartment so that upon being released from the plastic member, the perfume composition effectively suppresses malodors.

A second embodiment of the invention consists of the combination of the above specially-suited package and a liquid such as a detergent composition placed inside the package. In this second embodiment, the combination comprises: a container having at least one compartment for storing a liquid; a liquid composition such as a detergent, cleaning product, or a fabric care or personal care product disposed within this compartment comprising a first perfume composition; a dispensing opening in liquid communication with said at least one compartment; a closure for sealing the opening; and a plastic member which comprising a second perfume composition, wherein the plastic member is in communication with said compartment so that the second perfume composition effectively suppresses malodors by neutralization, modification, or masking. In fact, both perfume compositions may contribute to odor-suppression and, preferably, neither perfume composition has the same formulation of the other.

The present invention also separately relates to a perfume-impregnated material which releases fragrance materials or odor neutralizers in a gaseous phase whereby the fragrance materials or odor neutralizers mask malodors or neutralize or modify malodor-generating compounds and thus effectively suppress malodors.

All parts, percentages and ratios used herein are expressed as percent by weight unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

While the specification concludes with claims particularly pointing out and distinctly claiming the invention, it is believed that the present invention will be better understood from the following description taken in conjunction with the accompanying drawings in which:

Fig. 1 is a cross-sectional side view of an exemplary bottle made in accordance with the present invention;

Fig. 2 is an enlarged partial cross-sectional side view of the upper portion of the bottle of Fig.1;

Fig. 3 is a perspective view of a perfume-impregnated plastic member in the form of an annular disk suitable for use with the bottle of Fig. 1;

Fig. 4 is an enlarged partial cross-sectional side view of the upper portion of another preferred bottle made in accordance with the present invention, wherein the perfume-impregnated plastic member is provided as a cylindrical sleeve; and

Fig. 5 is an enlarged partial cross-sectional side view of the upper portion of yet another preferred bottle made in accordance with the present invention, wherein a perfume-impregnated plastic member in the form of a rod is provided.

DETAILED DESCRIPTION OF THE INVENTION

Definitions - The present detergent compositions comprise an "effective amount" or a "grease removal-improving amount" of individual components defined herein. By an "effective amount" of the diamines herein and adjunct ingredients herein is meant an amount which is sufficient to improve, either directionally or significantly at the 90% confidence level, the performance of the manual dishwashing composition against at least some of the target soils and stains. Thus, in a composition whose targets include certain grease stains, the formulator will use sufficient diamine to at least directionally improve cleaning performance against such stains.

By "light-duty liquid (LDL) detergent composition" it is meant a detergent composition which is employed in manual (i.e. hand) dishwashing.

By "kitchen articles" it is meant cookware, flatware, dishes and dishware, silverware and other articles commonly found in the kitchen and used for the preparation, consumption and serving of food as well as those articles used for cleaning up at the conclusion of a meal or other food preparation.

By "nitrogenous compounds" it is meant those compounds containing nitrogen and related to ammonia or ammonium. Such compounds include amines, polyamines, amine oxide surfactants, amides, surfactants in which the hydrophilic, polar groups are neutralized by an ammonium cation, alkanolamine solvents (e.g. monoethanolamine, diethanolamine, and triethanolamine) and other similar compounds which are typically used in detergent or cleaning compositions.

By "malodor" it is meant any detectable odor associated with and originating in any component of a detergent composition, particularly short-chain fatty acids or an amine or other nitrogenous compound related to ammonia or ammonium.

By "amine" it is meant any derivative of ammonia or ammonium in which one or more of the hydrogen atoms is replaced by an alkyl group, a cyclic hydrocarbon group, a fatty alkyl group or an aromatic group.

By "scent" it is meant any detectable odor associated with and originating in a fragrance material or an odor neutralizer.

By "volatility" it is meant the tendency of a liquid material to pass into the vapor state at a given temperature.

The present invention is directed to a package suitable for containing a liquid detergent, cleaning, fabric care, or personal care composition and a combination of such a package and the composition, particularly a liquid dishwashing detergent composition, having particular attributes. A package designed according to the present invention is particularly suited to suppress or mask the malodors generated by nitrogenous compounds found in such a composition contained inside the package. These nitrogenous compounds may be added to the liquid composition either intentionally to provide some performance benefit for the detergent, cleaning, fabric care or personal care composition, or they may be introduced inadvertently as impurities in the surfactant additives (particularly in amine oxide, betaine and polyhydroxy fatty acid amide surfactants) and in amine-containing polymers.

Referring to Fig. 1, an exemplary bottle 20 made in accordance with the present invention is illustrated. While the present invention will be described herein with respect to the exemplary bottle 20 for simplicity and clarity, the present invention can also be adapted for use with other types of hollow containers storing a material other than a liquid, such as granular or powdered materials. The bottle 20 comprises a hollow body 22 for storing a liquid 24 and has a closed bottom 26, at least one side wall 28, and a dispensing opening 30 disposed opposite the closed bottom 26. A male threaded finish 32 is disposed adjacent the opening 30 for removably receiving a female threaded closure 34 which prevents inadvertent spillage of the liquid 24 from the bottle 20. The threaded finish 32 can be integrally formed with the hollow body 22, or it can be provided as a separate structure which is attached to the hollow body 22 by an adhesive, friction welding, or any other method which provides a liquid tight seal between the finish 32 and the hollow body 22. The closure 34 preferably has an open position for dispensing the liquid 24 from the bottle 20 and a closed position for sealing the opening 30. The closure can be provided as is known in the art and may be of the flip top, turret cap, or push pull type, the latter being illustrated in Figs. 1 and 2. The cap can be formed from such materials as a copolymer of high density polyethylene and polypropylene by

injection molding. Alternatively, a simple threaded cap, such as that illustrated in U.S. Patent No. 4,981,239 to Cappel et al., can be provided or a snap-fitted closure, such as that described in U.S. Patent No. 5,865,331 to Jacobs, both patents being incorporated herein by reference, can be used. As will be appreciated, other closure and finish configurations can also be used which provide manual dispensing of the bottle's contents and provide a closed-end compartment for retaining the contents until dispensation is desired.

While the present invention is described herein with respect to a bottle having a single compartment, it will be appreciated that the present invention can be adapted for use with a multi-compartmented bottle, such as that described in U.S. Patent No. 4,678,103 to Dirksing which is fully incorporated herein by reference. Further, the present invention can be adapted for use with other types of hollow containers for storing liquids such as, LDLs, detergents for use in automatic dishwashing machines, laundry detergents, fabric softeners, deodorizers and refreshers, liquid hand soap, shampoo, after shave, cologne and personal deodorants, other personal care compositions, hard surface cleaners, and a variety of other home and personal care products. Further, the hollow container 22 can be provided with multiple finishes, closures, and side walls as desired. The hollow container 22 is preferably formed by blow molding from a thermoplastic, such as high density polyethylene, although other materials and manufacturing processes can be employed. For example, the bottle 20 can be formed by injection molding, rotational molding, thermoform molding, and the like using suitable materials known in the art.

In accordance with one aspect of the present invention, a perfume-impregnated plastic member in the form of a substantially round annular disk 36 is preferably disposed adjacent to the dispensing opening 30, between the closure 34 and the finish 32 of the bottle 20, wherein the annular disk 36 includes a perfume composition which effectively suppresses malodors by neutralization, modification, or masking. A significant amount of this suppression will preferably take place in the hollow container 22 as odor neutralizers and fragrance materials diffuse out and are released from the annular disk 36 and mask or neutralize the malodors that have diffused out of the liquid detergent composition and accumulated in the hollow container 22, particularly in the headspace 46 or on the interior of the side walls 28. More preferably, the annular disk 36 is disposed between the inner surface 38 of the closure 34 and the top surface 40 of the finish 32 such that the closure 34, when threaded onto the finish 32, secures the annular disk 36 in place. The annular disk 36 includes a hole 42 through which the liquid 24 can pass so that the liquid 24 can be dispensed from the hollow body 22 through the closure 34. The annular disk 36 is preferably sized

such that a sufficient portion of its surface area is exposed to the head space 46 (hereinafter referred to as the "active surface area") of the bottle 20 to effectively suppresses malodors generated by the liquid 24. As used herein, the phrase "head space" is intended to refer to the portion of the internal volume of the bottle 20 which is not occupied by the liquid 24. As will be appreciated, the volume of the head space 46 can vary from about 0 cm³ for a bottle which is fully filled to a maximum based upon the total internal volume of the bottle 20 as a function of the internal height 47 and other dimensions of the bottle 20. For a bottle 20 having a total internal volume of between about 25 ml and about 2000 ml, the active surface area of the annular disk 36 is preferably between about 1 cm² and about 1000 cm², and more preferably between about 1 cm² and about 10 cm². The annular disk 36 generally has an average thickness of between about 2 mm and about 20 mm, depending on the size of the bottle 20, the finish 32 and the closure 34. The ratio of the surface area of the perfume-impregnated plastic member which is exposed to the compartment for storing the liquid to the volume of the compartment is preferably between about 0.0005:1 cm²/ml and about 10:1 cm²/ml, more preferably between about 0.001:1 cm²/ml and about 0.01:1 cm²/ml.

The annular disk 36 is formed from a perfume-impregnated material 44 and may be formed into the disk-like shape by stamping. The perfume-impregnated material 44 contains an impregnating perfume composition which in turn comprises odor-neutralizers and optionally fragrance materials as set forth in more detail below. The perfume-impregnated material 44 can be formed from polymeric and composite materials and an impregnating perfume composition. Suitable materials include the fiber-reinforced composite materials and resins (particularly noted for their ability to contain an antimicrobial additive) disclosed in U. S. Pat. No. 5,919,554, to Watterson III et al., issued July 6, 1999, which is hereby incorporated by reference. Further suitable polymer materials include low density polyethylene, expandable polystyrene compositions, high density polyethylene, blended polyethylene and carbon black, polyene/alpha-olefin copolymers, poly-alpha-olefins, polyolefins, polyethylene oxides, olefin polymers and co-polymers, chlorinated PVC, polyepsilon caprolactone co-polymers, styrene acrylonitrile co-polymers, co-polymers of epsilon caprolactone with 1,4-butane diol, polyesters, chlorinated polyethylene, plasticized polyepsilon caprolactone co-polymers containing dimethyl phthalate plasticizers, maleic anhydride modified adducts of polyepsilon caprolactone polyols and ethylenically unsaturated monomer, polyurethane polymers having lactone backbones, polyurethane polyether resins wherein the resin is obtained by reacting a polyfunctional lactone with a long chain polyalkylene diol and a urethane precursor and

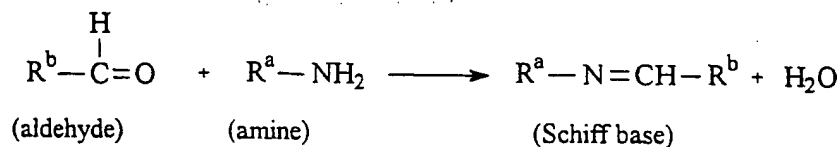
resins having polyurethane backbones, and mixtures thereof. All of these materials are discussed in greater detail in U. S. Pat. No. 4,521,541, to Rutherford et al., issued June 4, 1985, which is hereby incorporated by reference. Other perfume-impregnated materials suitable for use with the present invention can include foams, polymeric laminate structures comprising cardboard, cellulosic, or other material layers, and the like.

The perfume-impregnated material 44 will comprise from about 1% to about 30%, preferably from about 2 % to about 25 %, more preferably from about 5 % to about 20%, most preferably from about 8% to about 15%, by weight of impregnating perfume composition. The components of this impregnating perfume composition will now be discussed in detail.

a) Odor Neutralizers

Odor neutralizers work differently than the fragrance materials which are discussed at greater length below. They mask malodors by reducing the amount of the malodor-generating component which is responsible for the malodor. A suitable odor neutralizer is any chemical species that upon reacting with a malodor-generating compound (such as amines and other nitrogeneous compounds) yields products which generate little or significantly less malodor than the malodor-generating compound itself. Thus when the perfume-impregnated plastic member herein releases the odor neutralizer in a gaseous phase, the odor neutralizer reacts with one or more malodor-generating compounds to effectively suppress malodors.

A preferred species of odor neutralizers are aldehydes. It is well known that aldehydes react with amines in a Schiff reaction to produce a Schiff base and water:



In the above reaction, R^a and R^b are both aliphatic substituents. In the present invention the amine may be a diamine included for the benefits it provides on tenacious, hydrophobic and greasy soils. See the discussion of diamines below.

Schiff bases generate little or no malodor and thus by reacting an aldehyde with a amine they reduce the amount of the amine which is present to generate malodors. In the present invention, malodors emitted by amines in the liquid detergent composition and aldehydes released from the perfume-impregnated material 44 react in the gas phase or on the inner surfaces of the bottle 20. To prevent the amine from forming in excess in the headspace and to thus obtain the best possible malodor-suppression benefits, it is important that the rate of diffusion/release of the aldehydes from

the perfume-impregnated material 44 into the headspace 46 must exceed both the steady-state rate of migration of amine malodors from the liquid to gas phase and the rate of consumption of the aldehydes in the Schiff base reaction between amine and aldehyde.

Specific aldehydes suitable for use in the present invention include: para-tertiary-Butyl-alpha-methyl hydrocinnamic aldehyde, 4-(4-Methyl-4-hydroxyamyl)-3-cyclohexane-1-Carboxaldehyde, hydroxycitronellal, and alpha-methyl-beta-3,4-methylenedioxy-phenylpropionaldehyde, as well as most other aldehydes. For example, C₆-C₂₀ aldehydes, methyl nonyl acetaldehyde, citronellal, iso butyl citral, iso cyclo citral, mandarin aldehyde, methyl octyl acetaldehyde, oncidal, pre cyclemone B, iso dihydro lavendulyl aldehyde, oxy aldehyde, cyclac C, homo cuminic aldehyde 50%, hydrotropic aldehyde, 2, 6, nonadienal, triplal, vandor B, adoxal, anisic aldehyde, butyl cinnamic aldehyde, citronellyl oxy acetaldehyde, floralozone, florhydral, heliotropin, myrac aldehyde, lyral, cymal, amyl cinnamic aldehyde, hexyl cinnamic aldehyde, ethyl vanillin, helional, iris aldehyde, vanillin, cinnamic aldehyde, cuminic aldehyde, undecalactone, allyl caprylate, benzaldehyde, nonalactone, precyclemone B, prunolide, koavone, okoumal, phenyl acetaldehyde, and phenyl acetaldehyde dimethyl acetal are also useful herein. Many odor neutralizers, e.g. several different species of aldehydes, emit a characteristic scent and can also serve in the present invention as a fragrance material. From about 10% to about 100%, preferably from about 20% to about 75%, most preferably from about 30% to about 65%, by weight of the impregnating perfume compositions of the present invention will consist of an odor neutralizer.

b) Fragrance Materials

The impregnating perfume compositions in the perfume-impregnated material 44 contain fragrance materials which mask the presence of malodors emanating from malodor-generating compounds like amines. These fragrance materials mask the malodors by providing scents which compete with the malodors for access to the nasal receptor sites.

Under typical usage conditions, malodors associated with malodor-generating compounds such as amines and other nitrogenous components of a dish detergent product are liberated from the dish detergent product as soon as the detergent is exposed to air (e.g. the bottle is opened and the product is then applied to a dish surface or diluted further with water). Generally such malodors will have accumulated in the headspace 46 in the container between uses by the consumer. Once the malodors are free of the detergent container, they diffuse into the surrounding air, move to the nasal receptor sites and provide an adverse olfactory signal which consumers instantly associate with the product.

While not intending to be limited by theory, it is believed that the ability of fragrance materials contained in the present impregnating perfume compositions to mask malodors is related to the amount of time that the scents emanating from the fragrances require to diffuse into the air and hence move from the detergent packages to the nasal receptor sites. Thus the fragrance materials present in the impregnating perfume compositions are selected primarily on the basis of their volatility.

Highly volatile fragrance material are preferred fragrance materials for inclusion in the impregnating perfume compositions of the present invention. Highly volatile fragrance materials have lower boiling points than other substances and so the scents from these materials quickly diffuse into the air, and compete with the malodors to bind to the nasal receptor sites, becoming the first odors recognized and identified by the brain. Because the scents form the highly volatile fragrance materials are more volatile and arrive before the amine malodors at the nasal receptor sites, when the amine malodors do finally arrive the nasal receptor sites have already been occupied thus effectively masking the recognition of the amine malodors.

The present impregnating perfume compositions may comprise from about 0.5% to about 4%, preferably from about 1% to about 3%, by weight, of the highly volatile fragrance materials. Highly volatile fragrance material have a boiling point of below about 180°C, preferably below about 160°C, most preferably below about 140°C, under 1 atmosphere of pressure.

Most low molecular weight aldehydes (as discussed above), ketones, and esters have relatively low boiling points and are thus preferred examples of highly volatile fragrance materials suitable for use in the present invention. Examples of suitable ketones and esters can be found in U.S. Pat. No. 5,874,073 to Kaiser et al, issued February 23, 1999, which is hereby incorporated by reference. Further nonlimiting examples of suitable highly volatile fragrance materials and their respective boiling point values under 1 atmosphere of pressure include the following:

<u>Fragrance Material</u>	<u>Boiling Point (°C)</u>
Methyl acetoacetate	172
Cyclohexyl alcohol	161
3-Methyl-1-pentanol	151
1,3-Dimethylbutyl acetate	148
Isopropyl 2-methylbutyrate	138
ethyl-2-methylbutyrate	131

It is preferable that the present impregnating perfume compositions also constitute volatile fragrance materials. As used in this present invention, volatile fragrance materials are less volatile than the highly volatile fragrance materials and have a boiling point of between about 180°C and about 260°C, more preferably between about 185°C and about 240°C, most preferably between about 190°C and about 220°C, under 1 atmosphere of pressure.

The impregnating perfume compositions of the present invention are more effective at masking malodors originating in nitrogenous compounds and other compounds when both highly volatile and volatile perfume compositions are present. The combination of such perfume compositions effectively mask these malodors because they include highly-volatile fragrance materials, which arrive at the nasal receptor sites before the malodors, therefore effectively masking the malodors. However, it is possible that after sufficient time has passed and the malodors have arrived in the physical proximity of the nasal receptors sites, scents already resident in the sites may degrade or migrate out of them; thus giving the malodors an opportunity to bind with the sites and thereby making the odors perceptible to consumers. This is especially the case if there is a higher concentration of malodors or the malodors are more potent than the scents from highly volatile fragrance materials.

To prevent this, it is preferable to include volatile fragrance materials in the perfume composition which are not as volatile as the highly volatile fragrance materials. The scents from these fragrance materials should arrive either simultaneously or soon after the malodors and compete with the malodors for the sites vacated as scents emitted by the highly volatile fragrance materials degrade or migrate out of the nasal receptor sites.

The impregnating perfume compositions of the present invention may comprise from about 15% to about 40%, preferably from about 20% to about 35%, most preferably from about 20% to about 30%, by weight of volatile fragrance materials.

Nonlimiting examples of suitable volatile fragrance materials and their respective boiling point values under 1 atmosphere of pressure include the following:

<u>Fragrance Material</u>	<u>Boiling Point (°C)</u>
3,7-dimethyl-1,6-octadien-3-ol	198
3,7-dimethyl-7-hydroxyoctan-1-al	241
n-decyl aldehyde	215
benzaldehyde	179
anisic aldehyde	248

benzyl acetate	215
allyl hexanoate	185
methyl-2-aminobenzoate	237
2-cis-3,7-dimethyl-2,6-octadien-1-ol	227
3,7-dimethyl-trans-2,6-octadien-1-ol	230
3,7-dimethyl-6-octen-1-ol	225
2,6-dimethyl-7-octen-2-ol	208
2-phenylethyl alcohol	220
1-methyl-4-iso-propyl-1-cyclohexen-8-ol	219
1-1-methyl-4-iso-propenyl-6-cyclohexen-2-one	231
para-tertiary-amyl cyclohexanone	211
cyclohexanyl 2-tertiary butyl acetate	241
benzyl acetate	211

The boiling point of many perfume materials are disclosed in, e.g., "Perfume and Flavor Chemicals (Aroma Chemicals)," S. Arctander, published by the author, 1969, incorporated herein by reference. Other boiling point values can be obtained from different chemistry handbooks and databases, such as the Beilstein Handbook, Lange's Handbook of Chemistry, and the CRC Handbook of Chemistry and Physics. When a boiling point is given only at a different pressure, usually lower pressure than the normal pressure of one atmosphere, the boiling point at normal or ambient pressure can be approximately estimated by using boiling point-pressure nomographs, such as those given in "The Chemist's Companion," A. J. Gordon and R. A. Ford, John Wiley & Sons Publishers, 1972, pp. 30-36. When applicable, the boiling point values can also be calculated by computer programs, based on molecular structural data, such as those described in "Computer-Assisted Prediction of Normal Boiling Points of Pyrans and Pyrroles," D. T. Stanton et al, J. Chem. Inf. Comput. Sci., 32 (1992), pp. 306-316, "Computer-Assisted Prediction of Normal Boiling Points of Furans, Tetrahydrofurans, and Thiophenes," D. T. Stanton et al, J. Chem. Inf. Comput. Sci., 31 (1992), pp. 301-310, and references cited therein, and "Predicting Physical Properties from Molecular Structure," R. Murugan et al, Chemtech, June 1994, pp. 17-23. All the above publications are incorporated herein by reference.

While the shape of the annular disk 36 is preferred for the present invention, it will be appreciated that other shapes and configurations can be substituted for the annular disk 36. For example, a perfume-impregnated member in the shape of a polyhedral can be used. Further, the

perfume-impregnated member can be disposed at other locations of the bottle. For instance, as shown in Fig. 4, a cylinder or sleeve 48 can be disposed within the finish 32 such that the inner surface 50 of the sleeve 48 is exposed to the head space 46 of the bottle 120. The sleeve 48 can be secured in place using an adhesive or interference fit. Alternatively, the perfumed-impregnated member can be integrally formed with a portion of the closure 34 and/or the bottle 120 such the perfume-impregnated member is exposed to the head space 46 of the bottle 120. Processes which might be used to integrally form these closures and bottles include bi-injection molding and the like.

Referring to Fig. 5, yet another preferred bottle made in accordance with the present invention is illustrated. The bottle 220 includes a perfume-impregnated member in the form of a rod 52 which is attached to and extends from the closure 34 into the head space 46 of the bottle 220. The rod 52 can extend the entire internal height of the bottle 220, or less if desired, so that more of the rod 52 is exposed to the head space 46 as the liquid is dispensed from the bottle 220 and the volume of the head space 46 increases. The rod 52 can be formed integrally with the closure 34 or can be separately attached to the closure 34 by any suitable mechanical (e.g., interference fit) or chemical (e.g., adhesive) means as is known in the art.

The perfume-impregnated member may also take the form of the dipstick of a pump for dispensing the liquid disposed within a compartment of the package herein. In such a package, the perfume-impregnated member may be affixed to, or integrally formed with, a portion of the closure of the package, and would ordinarily extend the entire internal height, or most of the height, of the package to facilitate dispensing of the liquid.

In another embodiment, the perfume-impregnated member may be in the form of a flexible sheet, strip or bag that coats all or part of the internal surface of the compartment for storing the liquid in the package of the present invention. This could provide a perfume-impregnated member having much larger "active surface area" to effectively suppress malodors generated by the liquid disposed within the package.

Liquid Compositions

The package discussed above may be used to contain several different types of liquid compositions which will typically contain malodor-generating compounds which may be added either intentionally to provide some performance benefit for the detergent, cleaning, fabric care, or personal care composition or may be introduced inadvertently as impurities in one of the additives of the composition. These liquid compositions include LDLs, detergents for use in automatic dishwashing machines, laundry detergents, fabric softeners, deodorizers and refreshers, liquid hand soap,

shampoo, after shave, cologne and personal deodorants, other personal care compositions, hard surface cleaners, and a variety of other home and personal care products in which odor-emanating compounds like amines may be present and it is desirable to mask or suppress any malodors that they may generate. Thus many different types of liquid detergent compositions contain active ingredients which are also malodor-generating compounds. For example, a malodor-generating compound which is used in shampoos is a cationic polymer comprising nitrogenous monomeric units such as dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate etc. See e.g., U.S. Pat. No. 5,624,666, to Coffindaffer et al., issued April 29, 1997, which is hereby incorporated by reference.

Other malodor-generating compounds which can be useful in hair and skin-care products as well as other liquid detergents include polymers such as gums and resins which are primarily derived from natural sources; crosslinked nonionic polyacrylate polymers and crosslinked cationic polyacrylate polymers such as homopolymers, copolymers, and terpolymers of quaternary ammonium or cationic amine-substituted monomer units; polysaccharide polymers such as those derived from cellulose and starch; protein polymers; carboxylic acid polymers such as crosslinked acrylic acid homopolymers or copolymers; substituted or unsubstituted, linear or branched polyacrylamide polymers; copolymers of alkyl vinyl ethers and maleic anhydride; polyvinyl (N-pyrrolidones); silicone polymer materials (excluding the volatile silicone derivatives useful as a malodor-producing liquid carrier described hereinbelow) such as polydimethylsiloxane gums, silicone elastomers, siloxane gums, resin reinforced siloxanes, and crosslinked siloxane polymers; as well as silicone copolymers useful as hair styling polymers; and mixtures thereof, as disclosed in U.S. Pat. No. 5,919,400, to Kaiser et al., issued July 6, 1999, which is hereby incorporated by reference.

The malodor-generating amine-substituted groups mentioned above, e.g. $=N-C(=O)-$ monomer groups which provide dye-transfer inhibition benefits, can also be used in liquid fabric softener products. See e.g., U.S. Pat. No. 5,804,219, to Trinh et al., issued September 8, 1998, which is hereby incorporated by reference.

Amide-based nonionic surfactants such as hydrocarbylamidoalkylenesulfobetaine, which are often used in liquid detergents such as countertop, glass and surface cleaners, can also be a potent-source of malodors. See e.g., U.S. Pat. No. 5,108,660, to Michael, issued April 28, 1992, which is hereby incorporated by reference.

The liquid detergent products herein may themselves contain additional fragrance materials which not only provide additional malodor-suppression effects but also offer a way of incorporating into a consumer product two distinct and different "fragrances"—with one fragrance being found in the liquid detergent composition while the other is in the perfume-impregnated material 44. This could be a useful way to convey to a consumer, via an olfactory signal, that a detergent product has two distinct benefits, for example that its detergent composition is both tough on grease, while at the same time is gentle and mild to the skin.

These liquid detergent products and the malodor-generating compounds they contain which have been previously mentioned, are discussed only as examples to be illustrative of the breadth and benefits of the present invention, but are not meant to limit the scope of the malodor-suppression technology to the malodor-generating compounds or the liquid detergent products which have been specifically mentioned.

Such liquid detergents generally comprise an anionic surfactant, a solvent, an amine having a pKa with greater than about 8.0, and wherein the composition has a pH of from about 8.5 to about 12. The liquid detergent also preferably comprises a perfume composition comprising from about 30% to about 100% of an odor neutralizer capable of forming a Schiff base when reacted with the amine. Other liquid detergents herein comprise a nitrogen-containing polymer or a nitrogen-containing surfactant, wherein the nitrogen-containing surfactant is selected from the group consisting of amine oxides, amphoteric surfactants, glucose amides, and mixtures thereof and the amine is present as an impurity at a level of at least 1 ppm of the nitrogen-containing surfactants and the nitrogen-containing polymers.

The perfume compositions designed to suppress malodors such as nitrogenous malodors comprise fragrance materials which will now be set forth in more detail below. If desired, the present liquid compositions will comprise from about 0.01% to about 3%, preferably from about 0.01% to about 0.5%, more preferably from about 0.02% to about 0.2%, and most preferably from about 0.03% to about 0.08%, by weight of perfume composition.

The relation between the volatility of a fragrance material and its performance as well as the benefits and operative mechanisms of odor neutralizing aldehydes have been previously discussed above. Another important parameter of a fragrance material is the degree of hydrophobicity. Liquid detergent compositions of the present invention may be heavily diluted, having formulas containing as much as 80 % of water. Thus while the product is being stored, hydrophobic fragrance materials are more likely to concentrate themselves at the interface between the liquid detergent

composition and the headspace in the detergent container (e.g. squeeze bottle) in which the liquid dishwashing detergent is contained. When the product is used by a consumer, those fragrance materials which are more hydrophobic will be positioned on the liquid detergent-air interface and thus more readily evaporate into the air to provide pleasant fragrant signaling.

The degree of hydrophobicity of a fragrance material can be correlated with its octanol/water partitioning coefficient ("P"). The octanol/water partitioning coefficient of a fragrance material is the ratio between its equilibrium concentration in octanol and in water. A fragrance material with a greater partitioning coefficient P is more hydrophobic. Conversely, a fragrance material with a smaller partitioning coefficient P is more hydrophilic. The preferred fragrance materials of the present invention have an octanol/water partitioning coefficient P of 1000 or greater. Since the partitioning coefficients of the fragrance materials normally have high value, they are more conveniently given in the form of their logarithm to the base 10, log P.

The perfume compositions of the present invention may comprise from about 20 % to about 70 % , preferably from about 30 % to about 60 % , most preferably from about 40 % to about 55 % of fragrance materials which have ClogP values, as described hereinafter, of greater than about 2.5.

The logP values of many perfume ingredients have been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylog CIS), Irvine, Calif., contains many values, along with citations to the original literature. However, the logP values are most conveniently calculated by the "CLOGP" program, also available from Daylight CIS. This program also lists experimental logP values when they are available in the Pomona92 database. The "calculated logP" (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990, incorporated herein by reference). The fragment approach is based on the chemical structure of each perfume ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. The ClogP values, which are the most reliable and widely used estimates for this physicochemical property, are used instead of the experimental logP values in the selection of perfume ingredients which are useful in the present invention.

Nonlimiting examples of suitable fragrance materials and their respective ClogP values include the following:

Perfume Material

ClogP

Benzyl acetate	2.0
Ethyl-2-methylbutyrate	2.2
Furfuryl valerate	2.7
Isobutyl benzyl carbinol	2.9
para-Ethyl-alpha, alpha-dimethylHydro-cinnamaldehyde	3.4
Isobutyl caproate	3.8
4-tert.-butylcyclohexyl acetate	4.1

Perfume compositions which may be added to detergent compositions of the present invention may also include from about 0.10 % to about 4 %, preferably from about 0.15 % to about 2.5 %, most preferably from about 0.20 % to about 2.0 %, of the highly volatile fragrance materials described above. They may also comprise from about 30% to about 80%, preferably from about 30% to about 50%, more preferably from about 35% to about 50%, and most preferably from about 40% to about 45%, of volatile fragrance materials as described above.

Perfume compositions suitable for incorporation into the liquid detergents of the present invention are discussed at greater length in the PCT application of Kaiser et al. entitled "Perfume Compositions and Methods to Mask Amine Malodors," application number US 00/06606, having been filed on March 14, 2000, which is hereby incorporated by reference.

In addition, it may be desirable to incorporate into the present liquid detergent compositions complexing agents which have an internal cavity and are capable of forming complexes with the fragrance material ingredients of the perfume compositions. Preferred complexing agents are cyclodextrin molecules that are known for their ability to form complexes with perfume ingredients and have typically been taught as a perfume carrier. In addition, cyclodextrin molecules also appear to be surprisingly effective at reducing malodors generated by nitrogenous compounds, such as amines.

Thus in one embodiment of the present invention, the liquid detergent compositions comprise an anionic surfactant, a solvent and fragrance materials; wherein a portion of the fragrance materials are complexed with water-soluble cyclodextrin molecules while another portion are uncomplexed. Thus the present detergent compositions may contain fragrance materials which are complexed with cyclodextrin as well as free fragrance materials which when brought into the presence of cyclodextrin molecules are not incorporated into the molecule's cavity and remain as free molecules.

Further discussion of the use of cyclodextrin and fragrance materials in a liquid detergent composition may be found in the pending provisional application of Foley et al., entitled "Detergent Compositions with Perfume Complexes to Mask Malodors," having P&G Case No. 7806P2, Serial No. 60/204287, filed on May 15, 2000, incorporated herein by reference.

Components which perform useful functional, deterative or aesthetic benefits in a liquid detergent composition prepared according to the present invention will now be described *in seriatim*. These components described below are particularly suitable for formulating a LDL composition. Other components as well as their *ensemble* combination in various kinds of liquid detergent formulations are discussed in the numerous references which have been incorporated herein.

Diamines - As noted above, diamines may be used herein in detergent compositions in combination with deterative surfactants at levels which are effective for achieving at least a directional improvement in cleaning performance. In the context of a hand dishwashing composition, such "usage levels" can vary depending not only on the type and severity of the soils and stains, but also on the wash water temperature, the volume of wash water and the length of time the dishware is contacted with the wash water.

Since the habits and practices of the users of detergent compositions show considerable variation, the composition will preferably contain at least about 0.1%, more preferably at least about 0.2%, even more preferably at least about 0.25%, even more preferably still at least about 0.5%, by weight of said composition of diamine. The composition will also preferably contain no more than about 15%, more preferably no more than about 10%, even more preferably no more than about 6%, even more preferably no more than about 5%, even more preferably still no more than about 1.5%, by weight of said composition of diamine.

In one of its several aspects, this invention provides a means for enhancing the removal of greasy/oily soils by combining the specific diamines of this invention with surfactants. Greasy/oily "everyday" soils are a mixture of triglycerides, lipids, complex polysaccharides, fatty acids, inorganic salts and proteinaceous matter.

Thus diamines, in combination with amphoteric and anionic surfactants in the specific ratios discussed below, offer the benefit of improved grease and tough food cleaning which allows the elimination or reduction in the amount of divalent ions in the preferred embodiments of the present formula. This improved cleaning is a result of diamines' proclivity as a buffering agent to increase the alkalinity of the dishwashing composition. The superior rate of dissolution achieved by divalent ion elimination even allows the formulator to make hand dishwashing detergents, especially

compact formulations, at even significantly higher viscosities (e.g., 1,000 centipoise or higher) than conventional formulations while maintaining excellent dissolution and cleaning performance. This has significant potential advantages for making compact products with a higher viscosity while maintaining acceptable dissolution. By "compact" or "Ultra" is meant detergent formulations with reduced levels of water compared to conventional liquid detergents. For "compact" or "Ultra" formulations, the level of water is less than 50%, preferably less than 30% by weight of the liquid dishwashing detergent compositions. Said concentrated products provide advantages to the consumer, who has a product which can be used in lower amounts and to the producer, who has lower shipping costs. For compositions which are not meant to be concentrated, a suitable water level is less than about 85 %, more preferably less than about 70 % by weight of the liquid dishwashing detergent compositions.

Preferred organic diamines are those in which pK1 and pK2 are in the range of about 8.0 to about 11.5, preferably in the range of about 8.4 to about 11, even more preferably from about 8.6 to about 10.75. Preferred materials for performance and supply considerations are 1,3-bis(methylamine)-cyclohexane (pKa=10 to 10.5), 1,3 propane diamine (pK1=10.5; pK2=8.8), 1,6 hexane diamine (pK1=11; pK2=10), 1,3 pentane diamine (Dytek EP) (pK1=10.5; pK2=8.9), and 2-methyl 1,5 pentane diamine (Dytek A) (pK1=11.2; pK2=10.0). Other preferred materials are the primary/primary diamines with alkylene spacers ranging from C4 to C8. In general, it is believed that primary diamines are preferred over secondary and tertiary diamines.

Definition of pK1 and pK2 - As used herein, "pKa1" and "pKa2" are quantities of a type collectively known to those skilled in the art as "pKa." pKa is used herein in the same manner as is commonly known to people skilled in the art of chemistry. Values referenced herein can be obtained from literature, such as from "Critical Stability Constants: Volume 2, Amines" by Smith and Martel, Plenum Press, NY and London, 1975. Additional information on pKa's can be obtained from relevant company literature, such as information supplied by Dupont, a supplier of diamines.

As a working definition herein, the pKa of the diamines is specified in an all-aqueous solution at 25°C and for an ionic strength between 0.1 to 0.5 M. The pKa is an equilibrium constant which can change with temperature and ionic strength; thus, values reported in the literature are sometimes not in agreement depending on the measurement method and conditions.

Further discussion of the pK1 and pK2 values and diamines as well as examples of preferred diamines can be found in the PCT application of Joanna M. Clarke entitled "Diols and

Polymeric Glycols for Improved Dishwashing Detergent Compositions", having publication number PCT WO 00/46331, published August 10, 2000, incorporated herein by reference.

Anionic Surfactants - The anionic surfactants useful in the present invention are preferably selected from the group consisting of linear alkylbenzene sulfonate, alpha olefin sulfonate, paraffin sulfonates, alkyl ester sulfonates, alkyl sulfates, alkyl alkoxy sulfate, alkyl sulfonates, alkyl alkoxy carboxylate, alkyl alkoxyated sulfates, sarcosinates, taurinates, and mixtures thereof. An effective amount, typically from about 0.5% to about 90%, preferably about 5% to about 50%, more preferably from about 10 to about 30%, by weight of anionic deterative surfactant can be used in the present invention.

Suitable examples of anionic surfactants may be found in the PCT application of Chandrika Kasturi et al., entitled "Liquid Detergent Compositions Comprising Polymeric Suds Enhancers", having publication number PCT WO9927058A1, published June 3, 1999, which is incorporated above. Further examples of suitable anionic surfactants are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23. Suitable anionic surfactants may further be found in U.S. Pat. No. 5,415,814 issued 16 May 1995, to Ofosu-Asante et al., all of which are hereby incorporated by reference.

Amphoteric surfactants - The amphoteric surfactants useful in the present invention are preferably selected from amine oxide surfactants. Amine oxides are semi-polar surfactants and include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Further amphoteric surfactants, and amine oxides in particular, are disclosed in the PCT application of Joanna M. Clarke entitled "Diols and Polymeric Glycols for Improved Dishwashing Detergent Compositions", having publication number PCT WO 00/46331, published August 10, 2000, which is hereby incorporated in its entirety, by reference. Particular suitable for use herein,

because they are low-foaming, it may be desirable to use long chain amine oxide surfactants which are more fully described in U.S. Pat. Nos. 4,316,824 (Pancheri), 5,075,501 and 5,071,594, incorporated herein by reference.

Preferably the amphoteric surfactant is present in the composition in an effective amount, more preferably from about 0.1% to about 20%, even more preferably about 0.1% to about 15%, even more preferably still from about 0.5% to about 10%, by weight.

Secondary Surfactants - Secondary deterative surfactant can be selected from the group consisting of nonionics, cationics, ampholytics, zwitterionics, and mixtures thereof. By selecting the type and amount of deterative surfactant, along with other adjunct ingredients disclosed herein, the present detergent compositions can be formulated to be used in the context of laundry cleaning or in other different cleaning applications, particularly including dishwashing. The particular surfactants used can therefore vary widely depending upon the particular end-use envisioned. Suitable secondary surfactants are described in detail in the copending provisional patent application of Chandrika Kasturi et al., entitled "Liquid Detergent Compositions Comprising Polymeric Suds Enhancers", having publication number PCT WO9927058A1, published June 3, 1999, which is incorporated above.

Ratio of anionic to amphoteric to diamine

In the compositions of the present invention the ratio of the anionic surfactant: amphoteric: diamine is from about 100:40:1 to about 9:0.5:1, by mole, preferably the ratio of the anionic surfactant: amphoteric: diamine is from about 27:8:1 to about 11:3:1, by mole. It has been found that detergent compositions containing anionic surfactant, amphoteric surfactant and diamine in this specific ratio range provide improved low temperature stability, deliver better grease removal and tough food cleaning benefits at pH less than 12.5, and improved hard water cleaning.

In another aspect of the present invention the mole ratio of anionic surfactant to diamine of greater than 9:1, preferably greater than 20:1, has been found to give improved low temperature stability, deliver better grease removal and tough food cleaning benefits and improved hard water cleaning.

Solvents - A variety of water-miscible liquids such as lower alkanols, diols, polyols, ethers, amines and polymeric glycols which comprise ethylene oxide (EO) and propylene oxide (PO) groups and the like may be used in the present invention. Particularly preferred are the C1-C4 alkanols, diols and the above mentioned polymeric glycols.

When present the composition will preferably contain at least about 0.01%, more preferably at least about 0.5%, even more preferably still, at least about 1% by weight of the composition of solvent. The composition will also preferably contain no more than about 20%, more preferably no more than about 10%, even more preferably, no more than about 8% by weight of the composition of solvent.

Further examples of suitable solvents as well as their concentrations for use in a LDL compositions are disclosed in the PCT application of Joanna M. Clarke entitled "Diols and Polymeric Glycols for Improved Dishwashing Detergent Compositions", having publication number PCT WO 00/46331, published August 10, 2000, incorporated above and in the copending provisional patent application of Chandrika Kasturi et al., entitled "Liquid Detergent Compositions Comprising Polymeric Suds Enhancers", having publication number PCT WO9927058A1, published June 3, 1999, which is incorporated above.

Buffering Agents—Dishwashing compositions of the invention will be subjected to acidic stresses created by food soils when put to use, i.e., diluted and applied to soiled dishes. The compositions of the present invention will preferably have a pH of at least about 8.5, preferably at least about 10, more preferably, at least about 10.5; the compositions of the present invention will also have a pH of no more than about 12, preferably no more than about 11.5, more preferably no more than about 10.9. Because the detergent compositions of the present invention are largely alkaline, the detergent compositions will contain a buffering agent capable of providing a generally more alkaline pH in the composition and in dilute solutions. Dishwashing compositions of the present invention will thus contain from about 0.5% to 15%, preferably from about 1% to 12%, most preferably from about 2% to 10%, by weight, of a buffering agent. The pKa value of this buffering agent should be about 0.5 to 1.0 pH units below the desired pH value of the composition (determined as described above). Preferably, the pKa of the buffering agent should be from about 7 to about 12. Under these conditions the buffering agent most effectively controls the pH while using the least amount thereof.

Preferred inorganic buffers/alkalinity sources include the alkali metal carbonates, alkali metal hydroxides and alkali metal phosphates, e.g., sodium carbonate, sodium hydroxide, sodium polyphosphate.

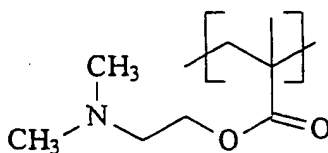
The buffering agent may be an active detergent in its own right, or it may be a low molecular weight, organic or inorganic material that is used in this composition solely for maintaining an alkaline pH. Preferred buffering agents for compositions of this invention are

nitrogen-containing materials. Further examples of suitable buffering agents may be found in the PCT application of Joanna M. Clarke entitled "Diols and Polymeric Glycols for Improved Dishwashing Detergent Compositions", having publication number PCT WO 00/46331, published August 10, 2000, incorporated above.

OPTIONAL DETERGENT INGREDIENTS:

Polymeric Suds Stabilizer - The compositions of the present invention may optionally contain a polymeric suds stabilizer. These polymeric suds stabilizers provide extended suds volume and suds duration without sacrificing the grease cutting ability of the liquid detergent compositions.

One preferred polymeric suds stabilizer is (N,N-dimethylamino)alkyl acrylate esters, namely



When present in the compositions, the polymeric suds booster may be present in the composition from about 0.01% to about 15%, preferably from about 0.05% to about 10%, more preferably from about 0.1% to about 5%, by weight. See PCT application of Chandrika Kasturi et al., entitled "Liquid Detergent Compositions Comprising Polymeric Suds Enhancers", having publication number PCT WO9927058A1, published June 3, 1999, which is incorporated above.

Builder - The compositions according to the present invention may further comprise a builder system. Because builders such as citric acid and citrates impair the stability of enzymes in LDL compositions, it is desirable to reduce the amounts of or completely remove the builder salts normally utilized in LDL compositions incorporating enzymes. When a detergent composition includes propylene glycol solvent as a part or a whole of the detergent's carrier, enzymes are more stable and higher amounts of builder salts may be added.

If it is desirable to use a builder, then any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylene-diamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine

pentamethylene-phosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Further discussion of suitable builders can be found in the PCT patent application of Joanna M. Clarke entitled "Diols and Polymeric Glycols for Improved Dishwashing Detergent Compositions", having publication number PCT WO 00/46331, published August 10, 2000, incorporated above.

If detergency builder salts are included, they will be included in amounts of from 0.5 % to 50 % by weight of the composition, preferably from 5% to 30%, and most usually from 5% to 25% by weight.

Enzymes - Detergent compositions of the present invention may further comprise one or more enzymes which provide cleaning performance benefits. Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases or mixtures thereof. A preferred combination is a detergent composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase. Enzymes when present in the compositions, at from about 0.0001% to about 5% of active enzyme by weight of the detergent composition. Preferred proteolytic enzymes, then, are selected from the group consisting of Alcalase[®] (Novo Industri A/S), BPN', Protease A and Protease B (Genencor), and mixtures thereof. Protease B is most preferred. Preferred amylase enzymes include TERMAMYL[®], DURAMYL[®] and the amylase enzymes those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Further non-limiting examples of suitable and preferred enzymes are disclosed in the PCT application of Joanna M. Clarke entitled "Diols and Polymeric Glycols for Improved Dishwashing Detergent Compositions", having publication number PCT WO 00/46331, published August 10, 2000, incorporated above.

Because hydrogen peroxide and builders such as citric acid and citrates impair the stability of enzymes in LDL compositions, it is desirable to reduce or eliminate the levels of these compounds in compositions which contain enzymes. Hydrogen peroxide is often found as an impurity in surfactants and surfactant pastes. As such, the preferred level of hydrogen peroxide in the amine oxide or surfactant paste of amine oxide is 0-40 ppm, more preferably 0-15 ppm. Amine impurities in amine oxide and betaines, if present, should be minimized to the levels referred above for hydrogen peroxide and preferably should be less than 1 ppm.

Magnesium ions

While it is preferred that divalent ions be omitted from LDL compositions prepared according to the present invention, alternate embodiments of the present invention may include magnesium ions.

It is desirable to exclude all divalent ions from the present LDL compositions, because such ions may lead to slower dissolution as well as poor rinsing, and poor low temperature stability properties. Moreover, formulating such divalent ion-containing compositions in alkaline pH matrices may be difficult due to the incompatibility of the divalent ions, particularly magnesium, with hydroxide ions.

Nonetheless, the presence of magnesium ions offers several benefits. Notably, the inclusion of such divalent ions improves the cleaning of greasy soils for various LDL compositions, in particular compositions containing alkyl ethoxy carboxylates and/or polyhydroxy fatty acid amide. This is especially true when the compositions are used in softened water that contains few divalent ions.

But in the present invention, these benefits can be obtained without the inclusion of divalent ions. In particular, improved grease cleaning can be achieved without divalent ions by the inclusion of organic diamines in combination with amphoteric and anionic surfactants in the specific ratios discussed above while enzymes have been shown to improve the skin mildness performance of the present LDL compositions.

If they are to be included in an alternate embodiment of the present LDL compositions, then the magnesium ions are present at an active level of from about 0.01 % to 1 %, preferably from about 0.015 % to 0.5 %, more preferably from about 0.025 % to 0.1 %, by weight. The amount of magnesium ions present in compositions of the invention will be also dependent upon the amount of total surfactant present therein, including the amount of alkyl ethoxy carboxylates and polyhydroxy fatty acid amide.

Preferably, the magnesium ions are added as a hydroxide, chloride, acetate, sulfate, formate, oxide or nitrate salt to the compositions of the present invention. Because during storage, the stability of these compositions becomes poor due to the formation of hydroxide precipitates in the presence of compositions containing moderate concentrations of hydroxide ions, it may be necessary to add certain chelating agents. Suitable chelating agents are discussed further below and in U.S. Pat. No. 5,739,092, issued April 14, 1998, to Ofosu-asante, incorporated herein by reference.

Chelating Agents - The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-tri-acetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanol diglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder. Similarly, the so called "weak" builders such as citrate can also be used as chelating agents.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Other Perfumes

In addition to the perfume and fragrance materials mentioned above, the present detergent compositions may also include various other natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can

comprise extremely complex mixtures of such ingredients. Further examples of perfume ingredients useful herein can be found in the PCT application: "Dishwashing Detergent Compositions Containing Organic Diamines for Improved Grease Cleaning, Sudsing, Low Temperature Stability and Dissolution", having publication number PCT WO 99/63034, published December 9, 1999, incorporated herein by reference. It should be noted that these additional ingredients which come under the heading "Other Perfumes" are included in addition to the perfume composition formulations discussed above.

Other Ingredients - The detergent compositions will further preferably comprise one or more deterative adjuncts selected from the following: soil release polymers, polymeric dispersants, polysaccharides, abrasives, bactericides and other antimicrobials, tarnish inhibitors, builders, enzymes, dyes, buffers, antifungal or mildew control agents, insect repellents, perfumes, hydrotropes, thickeners, processing aids, suds boosters, brighteners, anti-corrosive aids, stabilizers, antioxidants and chelants. A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, antioxidants, processing aids, and dyes or pigments. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous.

An antioxidant can be optionally added to the detergent compositions of the present invention. They can be any conventional antioxidant used in detergent compositions, such as 2,6-di-tert-butyl-4-methylphenol (BHT), carbamate, ascorbate, thiosulfate, monoethanolamine (MEA), diethanolamine, triethanolamine, etc. It is preferred that the antioxidant, when present, be present in the composition from about 0.001% to about 5% by weight.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of

C₁₃₋₁₅ ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Further, these hand dishwashing detergent embodiments preferably further comprises a hydrotrope. Suitable hydrotropes include sodium, potassium, ammonium or water-soluble substituted ammonium salts of toluene sulfonic acid, naphthalene sulfonic acid, cumene sulfonic acid, and xylene sulfonic acid.

Non-Aqueous Liquid Detergents

The manufacture of liquid detergent compositions which comprise a non-aqueous carrier medium can be prepared according to the disclosures of U.S. Patents 4,753,570; 4,767,558; 4,772,413; 4,889,652; 4,892,673; GB-A-2,158,838; GB-A-2,195,125; GB-A-2,195,649; U.S. 4,988,462; U.S. 5,266,233; EP-A-225,654 (6/16/87); EP-A-510,762 (10/28/92); EP-A-540,089 (5/5/93); EP-A-540,090 (5/5/93); U.S. 4,615,820; EP-A-565,017 (10/13/93); EP-A-030,096 (6/10/81), incorporated herein by reference. Such compositions can contain various particulate deterative ingredients stably suspended therein. Such non-aqueous compositions thus comprise a liquid phase and, optionally but preferably, a solid phase, all as described in more detail hereinafter and in the cited references.

The compositions of this invention can be used to form aqueous washing solutions for hand dishwashing. Generally, an effective amount of such compositions is added to water to form such aqueous cleaning or soaking solutions. The aqueous solution so formed is then contacted with the dishware, tableware, and cooking utensils.

An effective amount of the detergent compositions herein added to water to form aqueous cleaning solutions can comprise amounts sufficient to form from about 500 to 20,000 ppm of composition in aqueous solution. More preferably, from about 800 to 5,000 ppm of the detergent compositions herein will be provided in aqueous cleaning liquor.

The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent by weight unless otherwise specified.

EXAMPLES

Several annular disks are made from perfume-impregnated plastics of different compositions and then placed in the closure of a container, such as disclosed in Fig. 1, suitable for holding the liquid detergent compositions disclosed below. The plastics have the following compositions:

Disk A

50% low density polyethylene
30% ethylvinylacetate
20% hydroxycitronellal

Disk B

50% low density polyethylene
30% ethylvinylacetate
10% alpha-methyl-beta-3,4-methylenedioxy-phenylpropionaldehyde
5% Cyclohexyl alcohol
5% benzyl acetate

Disk C

50% low density polyethylene
30% ethylvinylacetate
15% lylal
5% Isopropyl 2-methylbutyrate

Light duty liquid dishwashing detergent compositions prepared according to the present invention are then dispensed into the container. During storage, the perfume-impregnated plastic disks release the odor neutralizers and fragrance materials in a gaseous phase so that they effectively suppress malodors generated by amines in the liquid detergent composition. The compositions are as follows:

Table I

	<u>Example 1</u>	<u>Example 2</u>	<u>Example 3</u>	<u>Example 4</u>
AE0.6S ¹	26.1	26.1	26.1	26.0
Amine oxide ²	6.5	6.5	6.5	6.5
Citric acid	2.6	2.6	2.6	—
Potassium carbonate	—	—	—	0.75
Sodium carbonate	—	—	—	1.75
Suds boosting polymer ³	0.2	0.2	0.2	0.2
Sodium cumene sulfonate	3.50	3.50	3.50	4.0
Propylene glycol	9.8	9.8	9.8	4.0
Nonionic surfactant ⁴	3.0	3.0	3.0	2.9
Diamine ⁵	0.50	0.50	0.50	0.50
Perfume composition ⁶	0.05	0.05	—	0.15
Water-soluble cyclodextrin & fragrances ⁷	—	—	0.5	
Water & minors	BAL.	BAL.	BAL.	BAL.
Total surfactant active	36 %	36 %	36 %	35.4%
Viscosity (cps @ 20°C)	780	780	780	650
pH @ 10%	10.8	10.8	10.8	10.8

1: Sodium C12-13 alkyl ethoxy sulfate containing an average of 0.6 ethoxy groups.

2: C₁₂-C₁₄ alkyl dimethyl amine oxide.

3: Polymer is (N,N-dimethylamino)ethyl methacrylate homopolymer

4: Nonionic may be either C11 Alkyl ethoxylated surfactant containing 9 ethoxy groups or C10 Alkyl ethoxylated surfactant containing 8 ethoxy groups..

5: 1,3 bis(methylamine)-cyclohexane.

6: The perfume composition is that described in table II.

7: The cyclodextrin and fragrance materials are selected as directed by the disclosure of the pending provisional application of Foley et al., "Detergent Compositions with Perfume Complexes to Mask Malodors," having P&G Case No. 7806P2, Serial No. 60/204287, filed May 15, 2000, incorporated herein by reference.

Table II

A perfume composition of the present invention is as follows:

<u>Fragrance Material</u>	<u>Weight %</u>
benzyl acetate	28.09
ethyl-2-methyl butyrate	0.70
ortho tertiary butyl cyclohexanyl acetate	14.04
para-Ethyl-alpha, alpha-Dimethyl Hydrocinnamaldehyde	0.28
P. T. Bucinal	42.13
3-Cyclohexane-1-Carboxaldehyde, 4-(4-Hydroxy-4-Methyl Pentyl)	14.04
Watermint	0.70

WHAT IS CLAIMED IS:

1. A package for storing a liquid, comprising:
a container having at least one compartment for storing a liquid;
a dispensing opening in liquid communication with said at least one compartment;
a closure for sealing said opening; and
a perfume-impregnated plastic member, wherein said perfume-impregnated plastic member is in communication with said compartment.
2. A package for storing a liquid according to claim 1 wherein the perfume-impregnated plastic member comprises a perfume composition comprising from about 10% to about 100% of an odor neutralizer, and said plastic member releases the odor neutralizer in a gaseous phase whereby the odor neutralizer is capable of reacting with one or more malodor-generating compounds to suppress malodors.
3. A package for storing a liquid according to claim 2 wherein one of the malodor generating compounds is an amine and the nonodiferous reaction product is a Schiff base.
4. A package for storing a liquid according to claim 3 wherein the odor neutralizer is selected from the group consisting of : para-tertiary-Butyl-alpha-methyl hydrocinnamic aldehyde, 4-(4-Methyl-4-hydroxyamyl)-3-cyclohexane-1-Carboxaldehyde, hydroxycitronellal, and alpha-methyl-beta-3,4-methylenedioxy-phenylpropionaldehyde, and mixtures thereof.
5. A package for storing a liquid according to claim 1 wherein the perfume-impregnated plastic member comprises a perfume composition comprising from about 0.5% to about 4% of fragrance materials having a boiling point of less than about 180°C, and said plastic member releases fragrance materials in a gaseous phase so that upon being released the fragrance materials effectively suppress malodors.
6. A package for storing a liquid according to claim 1 wherein the perfume-impregnated plastic member comprises a perfume composition comprising from about 15% to about 40% of

fragrance materials having a boiling point of between about 180°C and about 260°C, and said plastic member releases fragrance materials in a gaseous phase so that upon being released the fragrance materials effectively suppress malodors.

7. The package of claim 1 wherein said plastic member is disposed adjacent said dispensing opening.
8. A perfume-impregnated material comprising a perfume composition, wherein the perfume composition comprises from about 10% to about 100% of an odor neutralizer and said perfume-impregnated material releases the odor neutralizer in a gaseous phase whereby the odor neutralizer is capable of reacting with one or more malodor-generating compounds to suppress malodors.
9. A perfume-impregnated member according to claim 8 wherein the odor neutralizer is selected from the group consisting of para-tertiary-Butyl-alpha-methyl hydrocinnamic aldehyde, 4-(4-Methyl-4-hydroxyamyl)-3-cyclohexane-1-Carboxaldehyde, hydroxycitronellal, and alpha-methyl-beta-3,4-methylenedioxy-phenylpropionaldehyde, and mixtures thereof.
10. A perfume-impregnated member according to claim 8 wherein the perfume composition comprises from about 15% to about 40% of fragrance materials having a boiling point of between about 180°C and about 260°C.
11. The package of claim 1, wherein the surface area of said plastic member which is exposed to said compartment is between about 1 cm² and about 10 cm².
12. The package of claim 1, wherein the ratio of the surface area of said plastic member which is exposed to said compartment to the volume of said compartment is between about 0.0005: 1 cm²/ml and about 10:1 cm²/ml.
13. The package of claim 1, wherein the perfume-impregnated plastic member comprises a perfume composition comprising a fragrance material selected from the group consisting of methyl acetoacetate, cyclohexyl alcohol, 3-methyl-1-pentanol, 1,3-Dimethylbutyl acetate, isopropyl 2-methylbutyrate, ethyl-2-methylbutyrate, and mixtures thereof.

14. The package of claim 1, wherein said perfume-impregnated plastic member comprises a polymer material selected from the group consisting of low density polyethylene, expandable polystyrene compositions, high density polyethylene, blended polyethylene and carbon black, polyene/alpha-olefin copolymers, poly-alpha-olefins, polyolefins, polyethylene oxides, olefin polymers and co-polymers, chlorinated PVC, polyepsilon caprolactone co-polymers, styrene acrylonitrile co-polymers, co-polymers of epsilon caprolactone with 1,4-butane diol, polyesters, chlorinated polyethylene, plasticized polyepsilon caprolactone co-polymers containing dimethyl phthalate plasticizers, maleic anhydride modified adducts of polyepsilon caprolactone polyols and ethylenically unsaturated monomer, polyurethane polymers having lactone backbones, polyurethane polyether resins wherein the resin is obtained by reacting a polyfunctional lactone with a long chain polyalkylene diol and a urethane precursor and resins having polyurethane backbones, and mixtures thereof.

15. The package of claim 1, wherein said plastic member is an annular disk which is disposed adjacent to said dispensing opening.

16. The package of claim 15, wherein the average thickness of said disk is between about 2 mm and about 20 mm.

17. A package for storing a liquid, comprising:

a container having at least one compartment for storing a liquid;

a liquid disposed within said compartment comprising a first perfume composition;

a dispensing opening in liquid communication with said at least one compartment;

a closure for sealing said opening; and

a plastic member comprising a second perfume composition, wherein said plastic member is in communication with said compartment and said second perfume composition comprises an odor neutralizer, and said plastic member releases the odor neutralizer in a gaseous phase whereby the odor neutralizer is capable of reacting with one or more malodor-generating compounds to suppress malodors.

18. A package for storing a liquid detergent according to claim 17, wherein the liquid detergent further comprises:

a) an anionic surfactant;

b) a solvent;

c) an amine having a pKa of greater than about 8.0; and

wherein the first perfume composition comprises from about 30 % to about 100 % of an odor neutralizer which is capable of forming a Schiff base when reacted with an amine; and

wherein the composition has a pH of from about 8.5 to about 12.

19. A package for storing a liquid detergent according to claim 18, wherein the first perfume composition further comprises from about 0.10% to about 4% of fragrance materials having a boiling point of less than about 180°C.

20. A package for storing a liquid detergent according to claim 19, wherein the first perfume composition further comprises from about 20% to about 70% of fragrance materials having a ClogP value of greater than about 2.5.

21. A package for storing a liquid detergent according to claim 18, wherein the liquid detergent further comprises an amphoteric surfactant, a low molecular weight, malodor-generating organic diamine having a pK1 and a pK2, wherein the pK1 and the pK2 of said diamine are both in the range of from about 8.0 to about 11.5, and wherein the mole ratio of said anionic surfactant to said amphoteric surfactant to said diamine is from about 100:40:1 to about 9:0.5:1.

22. A package for storing a liquid detergent according to claim 17, wherein the liquid detergent further comprises nitrogenous compounds in which an amine is present as an impurity at a level of at least 1 ppm of the nitrogenous compounds.

23. A package for storing a liquid detergent according to claim 17, wherein the liquid detergent further comprises a nitrogen-containing polymer or a nitrogen-containing surfactant, wherein the nitrogen-containing surfactant is selected from the group consisting of amine oxides, amphoteric surfactants, glucose amides, and mixtures thereof and the amine is present as an impurity at a level of at least 1 ppm of the nitrogen-containing surfactants and the nitrogen-containing polymers.

24. A package for storing a liquid detergent according to claim 17, wherein the liquid detergent further comprises water-soluble cyclodextrin molecules.

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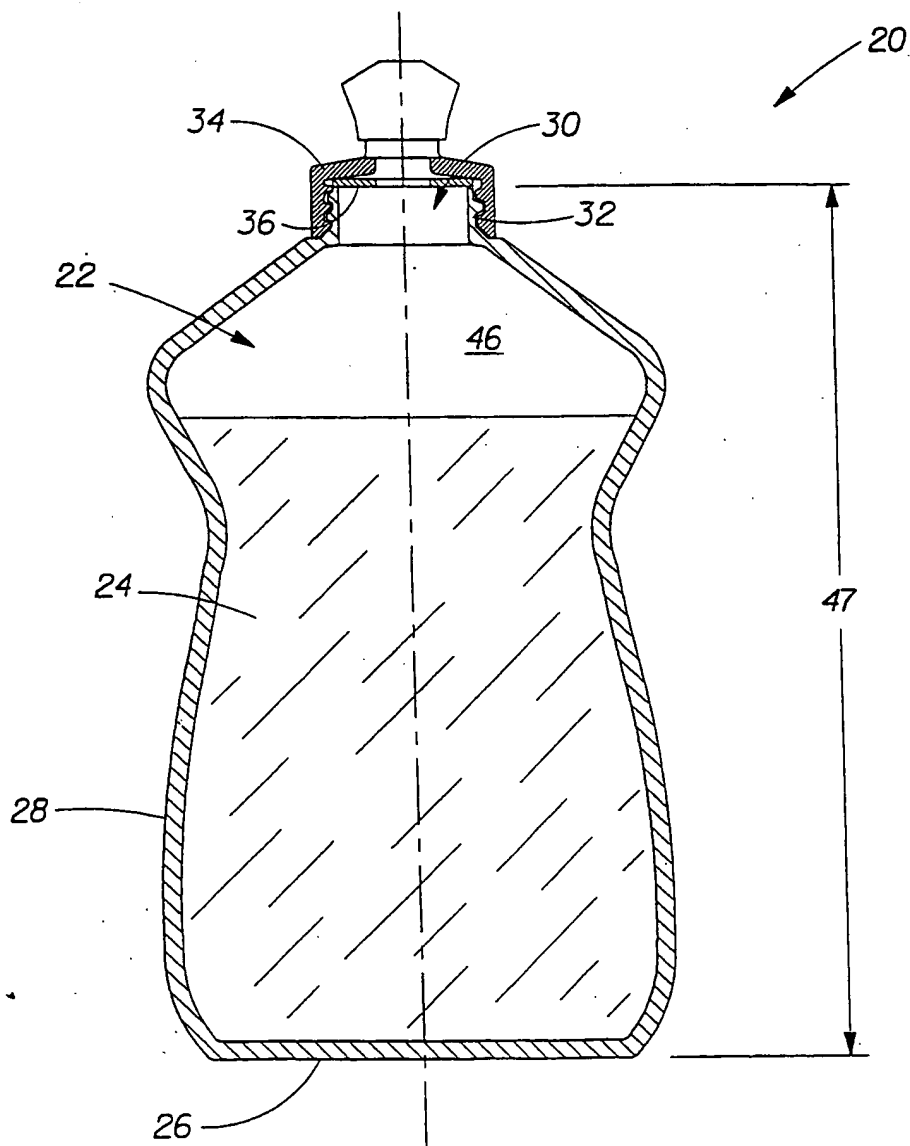


Fig. 1

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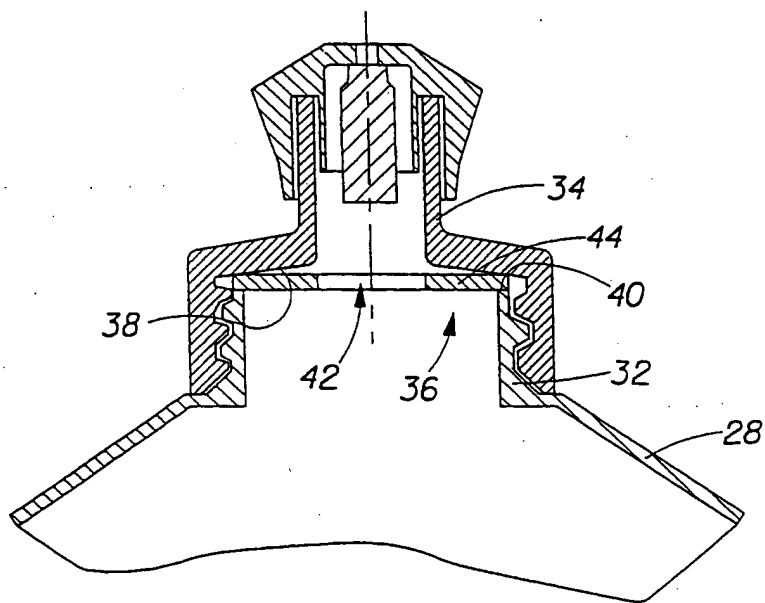


Fig. 2

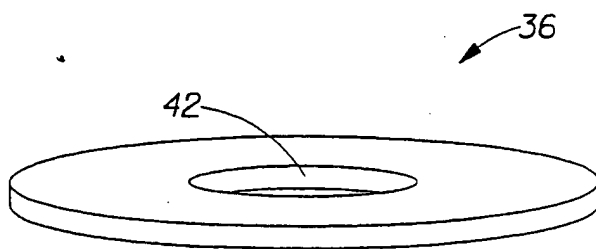


Fig. 3

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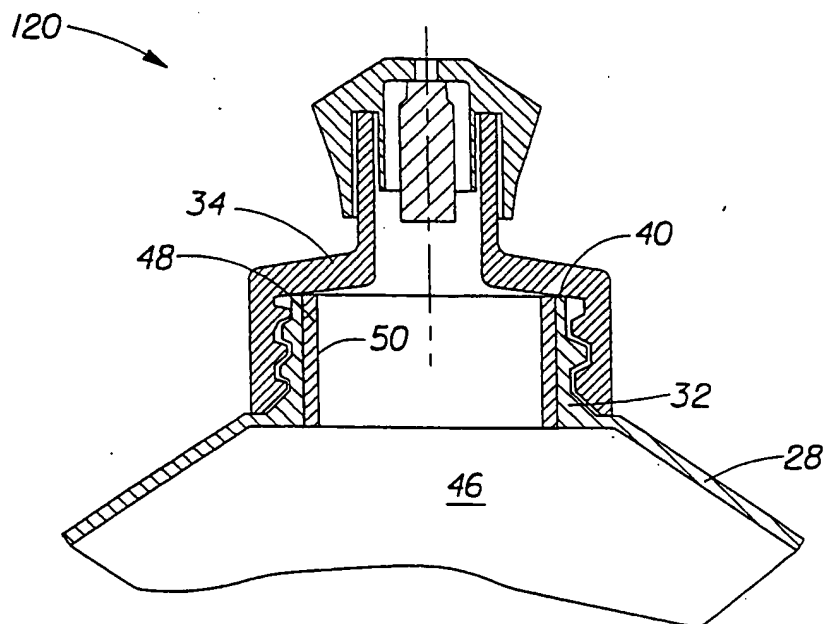


Fig. 4

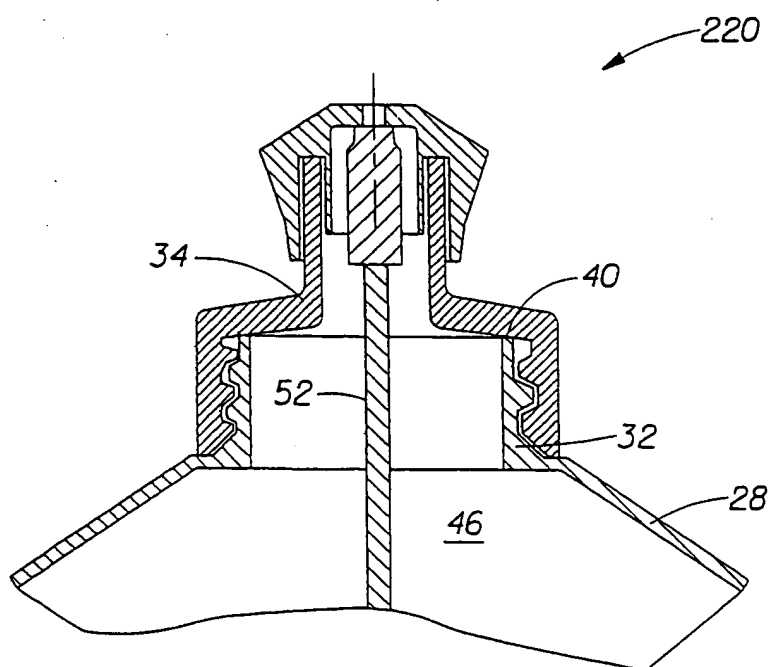


Fig. 5

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/27047

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B65D81/26 B65D51/24 C11D3/30 C11D3/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B65D C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 94 07757 A (UNILEVER) 14 April 1994 (1994-04-14) the whole document	1,7,11, 12,14-16 2-6, 8-10,13, 17-24
X	EP 0 258 991 A (CLOROX) 9 March 1988 (1988-03-09) page 2, line 1 - page 3, line 43 page 5, line 4 - line 20; figures 1,3,4	1,11,12, 14-16
P,Y	WO 00 55288 A (PROCTER & GAMBLE) 21 September 2000 (2000-09-21) cited in the application the whole document	2-6, 8-10,13, 17-24
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

18 January 2001

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/27047

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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